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Dipartimento di Chimica Inorganica, Analititca
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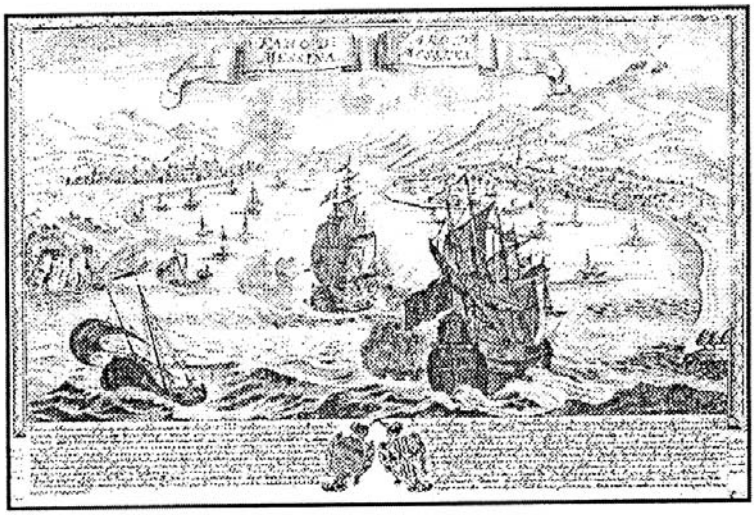
Atti Accademia Peloritana dei Pericolanti
Classe I di Scienze Fisiche
Matematiche e Naturali

WORKSHOP ON PLATINUM CHEMISTRY

ABSTRACTS



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α-CHIRAL PLATINUM ALKYLS

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A new synthetic route to α-chiral platinum alkyls, recently developed by us[1] and other groups[2], is based on the insertion of a carbene deriving from a diazocompound into a Pt-halogen or a Pt-carbon bond.

$$[Pt] - L + N_2CHR \rightarrow [Pt] - CHRL + N_2$$

$[Pt] = Pt(II)$ complex
$L =$ Halogen, CH_3
$R = COOEt,\ COPh,\ COOMenth,\ SiMe_3$

The reaction of the sterically hindered $N_2CHSiMe_3$ with optically active platinum complexes [PtX_2 (chiral diphosphine)] ($X = Cl, Br, I$) gives a pair of diastereomeric products [$PtX(CHXSiMe_3)$(chiral diphosphine)], one being largely predominant (up to 15:1 diastereomeric ratio) in some cases. For both the products [$PtBr(CHBrSiMe_3)$(S,S-chiraphos)] and [$PtCl(CHClSiMe_3)$(S,S-skewphos)], the major isomer has been separated in pure form and the absolute configuration at the α carbon has been determined by x-ray crystal structure.

The behaviour of the $PtCHXSiMe_3$ group (X=halogen) with respect to epimerization and halogen substitution has been explored.

These compounds are examples of α-chiral platinum alkyls with a single, assigned and stable configuration at the α carbon, which is a relevant character for the potential use of this class of compounds to investigate the mechanism of fundamental organometallic reactions and of asymmetric transformations catalysed by transition metals complexes.[3]

During this study, we observed that the group $Pt-CHXSiMe_3$ (X =halogen) can easily undergo desilylation in the presence of water, with loss of chirality:

$$[Pt]-CHXSiMe_3 \xrightarrow{H2O} [Pt]-CH_2X$$

This reaction can be used as a convenient alternative synthesis of chloromethylplatinum complexes avoiding the use of CH_2N_2.

When $N_2CHSiMe_3$ reacts with a substrate containing a $Pt-Me$ bond, both the chiral $PtCHMe-SiMe_3$ and the non chiral $Pt-CH_2SiMe_3$ groups can be formed, depending on the reaction conditions.

A mechanism for these transformations will be proposed on the basis of experimental observations.

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